**A MINIATURE MONOLITHIC SPATIAL HETERODYNE SPECTROMETER FOR REMOTE RAMAN AND LIBS, 1D RAMAN IMAGING, AND IN-SITU RAMAN USING A DRONE CAMERA DETECTOR.**

Abigail Waldron[1], Arelis Colón[1], J. Chance Carter[2], Shiv Sharma[3], and S. Michael Angel[1], [1]University of South Carolina, Columbia, SC 29208, USA. (SMANGEL0@mailbox.sc.edu), [2]Lawrence Livermore National Laboratory, Livermore, CA 94550-5507, USA. [3]Univeristy of Hawaii, Honolulu, HI 96822, USA.

**Overview:** Raman spectroscopy is a vibrational technique and is a good candidate for planetary exploration, because it can be used to make remote geochemical measurements and to identify organic and inorganic biomarkers of life [1]. In previous work we described a spatial heterodyne Raman spectrometer (SHRS) that is small with no moving parts, and ideally suited for planetary spacecraft and rovers. The SHRS is based on a fixed grating interferometer and has high spectral resolution and high light throughput. The resolution of the SHRS is not dependent on a slit, so miniature systems can be made without sacrificing resolution. A miniature SHRS we recently described used a cell-phone detector and imaging optics with 2.5 mm sized diffraction gratings, and the performance was compared to a standard laboratory instrument [2]. In this paper we describe an extension of this idea, using monolithic construction techniques to make a solid state SHRS (mSHRS), which is very stable and better suited to space applications. The mSHRS spectrometers are about 35x35x25mm in size, weigh about 80g, with a 3500 $cm^{-1}$ spectral range and 4-5 or 8-9 $cm^{-1}$ resolution, depending on the device.

**Experimental:** Fig. 1 shows a monolithic SHRS next to a US Quarter for scale. The mSHRS interferometer consists of two 15 mm by 15 mm diffraction gratings, a BK7 50:50 cube beam splitter, and two angled BK7 spacers, cemented together with UV cured epoxy into a solid piece. The device pictured was designed for 532 nm and has ~8-9 $cm^{-1}$ resolution with a 3500 $cm^{-1}$ spectral range using a 2048 pixel CCD.

**Results and Discussion:** The basic design and operation of the SHRS has been discussed previously. In the interferometer, collimated light is passed through a 50/50 beam splitter, diving the beam into two parts which are directed onto tilted diffraction gratings. After being diffracted off the gratings, the beams recombine at the beamsplitter as crossing wave fronts. The gratings are titled at an angle, $\theta_L$, such that a particular wavelength, the Littrow wavelength, $\lambda_L$, is retro-reflected and recombined so that no interference pattern is produced. For any wavelength other than Littrow, the crossed wave fronts will generate a fringe pattern, which is imaged onto the CCD to produce a fringe image.

The high throughput and multiplex advantage of the mSHRS allows Raman spectra to be measured using low-cost, uncooled CMOS, such as those used as cameras on commercial drones. To test this idea, we used a drone (Mavic Platinum Pro 2) to image the fringes produced by the gratings of the mSHRS. Figure 2 shows Raman spectra of (a) sulfur, (b) potassium perchlorate, and (c) ammonium nitrate using the mSHRS pictured in Fig. 1 using the drone camera (shown as inset, Fig. 2). The inserts in Figure 2 show the Raman interferograms for each spectrum. The SNR of the measured Raman spectra were comparable to similar measurements using a scientific grade, cooled CCD.

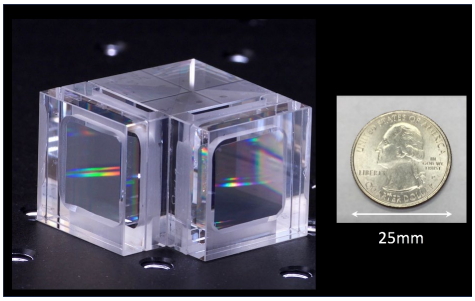


**Fig 1.** Monolithic spatial heterodyne Raman spectrometer on scale with a US Quarter.

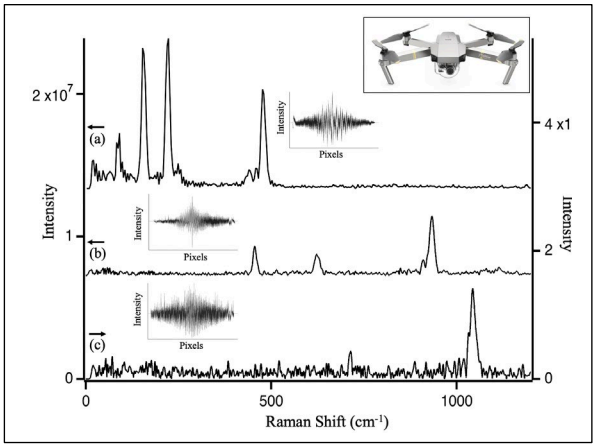


**Fig 2.** Raman spectra of (a) sulfur, (b) potassium perchlorate, and (c) ammonium nitrate with a mSHRS using the CMOS camera on a Mavic Platinum Pro 2 Drone. The cross sections for each spectra are shown in the inserts. Top right inset: picture of the drone used.

Drone Raman measurements are greatly simplified if non imaging collection optics are used. Thus, we tested the mSHRS for remote Raman measurements with samples at a distance of ~5m, with no imaging collection optics, using only the mSHRS' 15-mm gratings to collect Raman scattered light. At this distance, the collection solid angle of the mSHRS is $9x10^{-6}$ sr, so relatively

high laser power, 500 mW at 532 nm, was used to compensate, with a 300 sec exposure time.

Fig. 3 shows remote Raman spectra of (a) potassium perchlorate, (b) barite, and (c) acetaminophen measured in this way with the 150 gr/mm mSHRS. The SNR is relatively poor, not surprising considering the small collection optic. However, this does suggest the possibility of building extremely small remote Raman spectrometers for use in small spacecraft or drones of the types that might be used on the outer planets or comets.

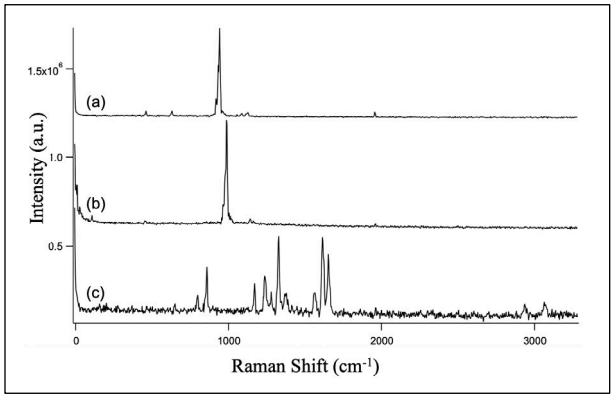


**Fig 3.** Remote Raman spectra at ~5 m: (a) $KClO_4$, (b) $BaSO_4$, and (c) acetaminophen using a mSHRS.

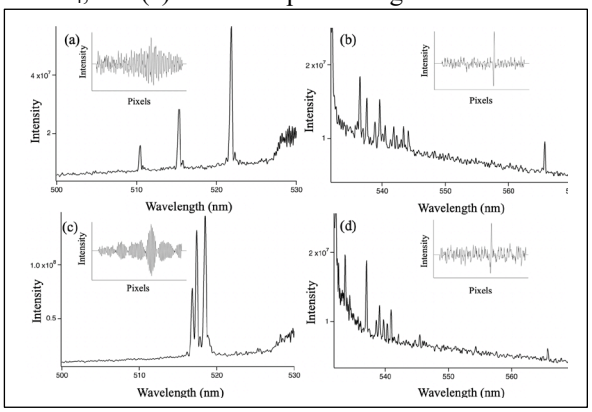


**Fig. 4.** Remote LIBS spectra of (a) copper, (b) iron, (c) manganese, and (d) magnesium with a mSHLS.

To demonstrate the mSHS for LIBS, we measured remote LIBS spectra at 4.5. Figure 4 shows remote LIBS spectra of some metals using the same mSHS that we used for the Raman measurements, and illustrate the high resolution and large spectral range of the mSHS.

Raman imaging is useful for heterogenous samples, and to improve SNR for mixed samples. Figure 5 shows the non-spatially resolved Raman fringe image (FI, b) of the stacked cuvettes sample compared to the spatially resolved, 1D Raman fringe image (FI, a), both measured using the mSHRS. Spatially resolved images are acquired by using a cylindrical lens to form an image of the sample onto the gratings of the mSHRS. The samples were $Na_2SO_4$ and $NaNO_3$ contained in separate cuvettes (upper right). The laser was defocused to illuminate both samples. A row by row FFT was used to obtain Raman spectra from each fringe image. The Raman spectrum from the non-imaged fringe image (FI, b) is shown in 5c, and shows the combined signal of both the sulfate and nitrate bands. But spatially resolved spectra (Fig. 5a, b) are obtained from the 1D spatially resolved fringe image, by taking a separate FFT for regions of the spatially resolved 1D fringe image that correspond to each cuvette. The spatially resolved spectra, from the 1D images, show clear separation of the components in the two cuvettes, at a spatial resolution that is only limited by the CCD pixel size. The signal to noise ratio (SNR) for the Raman spectra collected via 1D imaging (5 a,b) was higher than the spectra without imaging (5c), 288 and 120 for sodium nitrate and sodium sulfate respectively in the 1D spectra, versus 85 and 59 for the unresolved spectra. The increased SNR in the 1D resolved spectra is the result of reduced shot noise in each spectrum. As with any other interferometer, in the mSHS shot noise is equally distributed throughout all parts of the spectrum, so noise from strong bands reduces the SNR of weaker bands. However, in the spatially resolved spectra, from the 1D images, shot noise from one component does not contribute to noise in the other component.

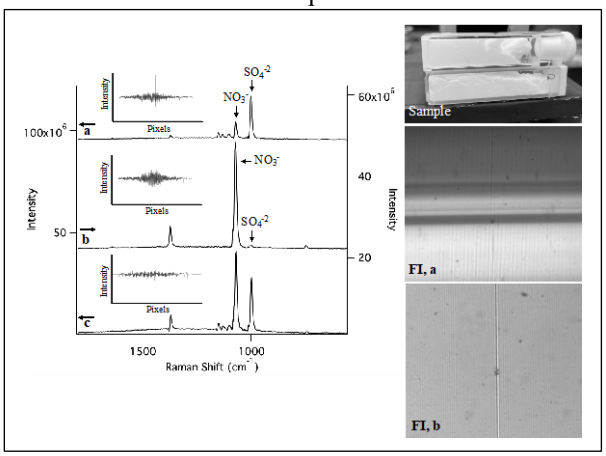


**Fig. 5.** 1D imaging with a mSHRS (150 gr/mm, 616.5 nm $\lambda_L$) of $Na_2SO_4$ and $NaNO_3$.

**Conclusion:** Monolithic spatial heterodyne Raman spectrometers of about 35x35x25mm in size, weighing ~80g, with >3500 $cm^{-1}$ spectral range and up to 4-5 $cm^{-1}$ resolution are described.

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**References:** [1] Angel S. M. et al., *Appl. Spectrosc., 66,* 137-150 (2012).[2] Barnett P. et al., *Appl Spectrosc*., *71*, 988-985 (2017). [3] Waldron A. et al., *Appl. Spectrosc.,* DOI:10.1177/0003702820936634 (2020).